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COULOMB CORRELATION EFFECTS IN QUASI-ONE-DIMENSIONAL CONDUCTORS

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We review recent results on the role of electron-electron (e-e) interactions – "correlation effects" – in quasi-one-dimensional conductors. Within the Peierls-Hubbard model, we examine the consequences of short range (on-site U and nearest neighbor V) e-e interactions for ground state properties, nonlinear excitations, and optical absorption. Our techniques include quantum Monte Carlo and weak and strong coupling perturbative arguments.

1. INTRODUCTION

Much of the current debate on quasi-one-dimensional conductors focuses on the relative importance of electron-phonon (e-p) and electron-electron (e-e) interactions. Experimentally, in the context of conducting polymers, for example, the observed [1] dimerization/ bond alternation in trans-polyacetylene proves the existence of e-p interactions. On the other hand, several recent observations – including the ordering of excited states in finite polyenes [2] and, in trans-$(CH)_x$, the appearance of negative spin densities on alternate carbon atoms [3,4] and the strong shift of the "neutral soliton" absorption from mid-gap [5] – clearly establish the significant presence of e-e interactions. Theoretically, the relative simplicity of the pure e-p models – such as the SSH [6] Hamiltonian for $(CH)_x$ – and their predictions of localized, nonlinear "soliton" excitations have understandably led to an emphasis on these models. Yet, in view of the experiments [2-6], one clearly requires a thorough study of the role of e-e interactions – typically called "correlation effects" – in all their many-body complexity in order to be certain of the modeling of these systems. In the present note we review briefly some of our own recent results on e-e interactions; the necessary details and a more complete bibliography of the relevant literature are provided in the references. In the ensuing sections, we first introduce the "Peierls-Hubbard" model, then quote some quantum Monte Carlo results for the ground state and nonlinear excitations, and close by mentioning some work in progress aimed at understanding the optical absorption of these systems in the weak and strong e-e interaction limits. Unfortunately, space does not permit the inclusion of some limited but interesting results on long-range interactions [7].

2. THEORETICAL APPROACH AND MODEL

To obtain a clear theoretical understanding of the interplay of e-p and e-e interactions, it is essential to study as exactly as possible a well-defined model with a limited number of parameters. We therefore focus on the "Peierls-Hubbard" Hamiltonian, $H = H_{1-e} + H_{e-e}$, where

$$H_{1-e} = \frac{1}{2M}\sum_i P_i^2 + \frac{K}{2}\sum_i (u_i - u_{i+1})^2 + \sum_{i,\sigma}(t_0 + \alpha(u_i - u_{i+1}) + (-1)^i t_1)(c^\dagger_{i+1,\sigma}c_{i,\sigma} + c^\dagger_{i,\sigma}c_{i+1,\sigma}) \qquad (1.a)$$

and

$$H_{e-e} = \frac{U}{2}\sum_{i,\sigma} n_{i,\sigma}n_{i,-\sigma} + V\sum_i n_i n_{i+1}\ , \qquad (1.b)$$

where $c_i^\dagger$ (c_i) creates (annihilates) an electron at site i and $n_{i,\sigma} = c^\dagger_{i,\sigma}c_{i,\sigma}$ and $n_i = \sum_\sigma n_{i,\sigma}$. This Hamiltonian – perhaps generalized to include intra- molecular phonons coupled to the electrons – serves as a theoretical starting point for a variety of quasi-one-dimensional systems, including materials with differ-

ent effective band-fillings, $\rho \equiv N_e/N$, where N_e is the number of electrons and N the number of sites. In the half-filled case ($\rho = 1$), the model applies to π-conjugated conducting polymers, to mixed stack charge transfer salts [8], and to M-TCNQ ($M = Li, Na, K, Rb$) salts. An example of another band filling is TTF-TCNQ, which at 19 Kb is near the $\rho = 2/3$ limit [9]. Of course, the ranges of parameters can differ for different systems. For conducting polymers, one expects rough values to be $t_0 \sim 2.5eV, U \sim 10eV, V \sim 5eV$, and $\lambda \equiv (2\alpha^2)/(\pi K t_0)$, the dimensionless e-p coupling constant, in the range 0.1-0.2. For the M-TCNQ salts, one has much smaller bandwidths ($t_0 \sim 0.1 - 0.3eV$), smaller e-e interactions ($U \sim 1.5eV$ and $V \sim 0.5eV$), and comparable λ (0.1-0.3).

Despite the nominal prohibition against discussing conducting polymers – as opposed to other quasi-one-dimensional conductors – at this conference, both for continuity with our previous work and to emphasize the emerging unity of the theoretical description of these systems we shall focus here on applications of H to conducting polymers, taking trans-$(CH)_x$ and cis-$(CH)_x$ or polythiophene as the respective prototypes for the degenerate and non-degenerate ground state cases. In the physical context of $(CH)_x$, the displacements (u_n) of the (CH) units along the chain are coupled (with strength α) to the hopping term which transfers π-electrons between adjacent sites, and the Hubbard U and V model the (short range) Coulomb repulsion between electrons on, respectively, the same site and nearest neighbor sites. Note that t_1 represents an extrinsic "dimerizing" modulation to the hopping integral, so that $t_1 = 0$ for polymers with two-fold degenerate ground states (e.g., trans – $(CH)_x$ and $t_1 \neq 0$ for polymers with non-degenerate ground states [10] (e.g., cis – $(CH)_x$ or polythiophene). Typically, calculations are carried out in the adiabatic limit, in which the quantum nature of the phonons is ignored and H is treated as an energy functional, to be minimized over phonon coordinates. Treating the single particle Hamiltonian in this manner leads [6] to the predictions that the ground state is indeed dimerized (and that there exists a corresponding $2k_F$ bond order wave (BOW)) and that, for $t_1 = 0$, the nonlinear excitations include kink solitons [6] (K^0, K^+, and K^-) and polarons [10-13] (P^+ and P^-), whereas for $t_1 \neq 0$, there are only polarons and bipolarons [8,10-11] (BP^{--}, BP^{++}, and BP^0, which is nothing but a singlet exciton in which the charges are bound by strong e p coupling).

3. QUANTUM MONTE CARLO STUDIES

Since our results on the effects of short range e-e interactions have been discussed extensively elsewhere [14], here we simply recall two sets of points relevant to our present discussion. First, dimerization does persist in the presence of correlations, and (for the relevant range of e-p coupling) is in fact enhanced (for $V = 0$) from its value when only H_{1-e} is present. Adding V further enhances the dimerization. Importantly, this proves that the Hartree-Fock approximation, which predicts [15] the absence of a BOW above $U/t_0 \sim 2$, fails qualitatively for even moderately strong e-e interactions. Second, the solitons of trans – $(CH)_x$ remain stable, with the important qualitative differences that the degeneracy between K^0 and K^* is broken and, consistent with the ENDOR data [3,4], negative spin densities appear on alternate carbons in the case of the neutral soliton. In addition, soliton doping persists, i.e., the K^+K^+ state is favored over the doubly charged dimer. To the extent that they overlap, these results are entirely consistent with those obtained in related Monte Carlo [16] and other exact [17-18] or renormalization group [19] many-body methods.

4. OPTICAL ABSORPTION IN THE PRESENCE OF ELECTRON-ELECTRON INTERACTIONS

In Section III we have already indicated briefly that the striking nonlinear excitations of the single particle theory are expected to remain relevant at least for some properties even in the presence of relatively strong e-e interactions. Since within the single particle theory perhaps the clearest signatures of these excitations are their intra-gap optical absorptions, observable both in doped samples and in photo-induced photoabsorption, it is essential to understand how these

intra-gap features change in the presence of e-e interactions. Unfortunately, this is a hard problem, for it in effect requires knowledge of the many-particle wave functions of the excited states in addition to the ground state. Indeed, an important challenge to theory over the next few years is to improve on the semi-quantitative discussion given below of the weak and strong e-e interaction limits.

We begin by recalling briefly the results for $\alpha(\omega)$, the optical absorption as a function of photon frequency (ω), in the single particle theory. For kink solitons (see, eg., Ref. 20), associated with the single localized electronic level at mid-gap is a strong intra-gap absorption having, in the strictly one dimensional continuum model, a $(\omega-\Delta_0)^{-1/2}$ singularity at the absorption edge $\omega = \Delta_0$. By the optical sum rule, the strength in this absorption is removed from the inter-band transition, leading to a "bleaching" above $\omega = 2\Delta_0$. For polarons (see Fig. 1 and Ref. 21) the two localised electronic levels (at $\pm\omega_0$) lead to three distinct intra-gap absorptions, for which analytic expressions are available [21] in the continuum limit: (1) α_1, a δ-function transition at $\omega = 2\omega_0$; (2) α_2, a (strong) low energy feature exhibiting a $(\omega - (\Delta_0 - \omega_0))^{-1/2}$ singularity at the absorption edge $\omega = \Delta_0 - \omega_0$; and α_3, a (weak) high energy feature which vanishes as $(\omega - (\Delta_0 + \omega_0))^{+1/2}$ at the absorption edge $\omega = \Delta_0 + \omega_0$. The relative integrated intensities, as functions of ω_0, the location of the localized electronic levels, are shown in Fig. 2. For charged bipolarons [21], there are also two localized electronic levels (at $\pm\omega_0'$, with $\omega_0' < \omega_0$ for the same bare parameters in H) but the occupancy of these levels (fully occupied for BP^{--}, empty for BP^{++}) precludes the δ-function transition at $\omega = 2\omega_0'$. Thus the two intra-gap transitions for the bipolaron are the (strong) transition α_2 at $\omega = (\Delta_0 - \omega_0')$ and the (weak) α_3 at $\omega = \Delta_0 + \omega_0'$.

To discuss the changes due to e-e interactions, we focus on the cases of the kink and the bipolaron, as these have been of greatest recent experimental interest. Furtl.er, for simplicity we consider only the effects of U (and in some indicated cases, V). In the case of the kinks, for weak e-e coupling involving U only, we find [22] (using first order perturbation theory) that the optical transition energy, $(TE)^0$, associated with the presence of a neutral kink shifts upward from mid-gap toward the band edge (consistent with earlier experiments [5]) to $(TE)^0 = \Delta_0 + U/3\ell_K$, where ℓ_K is the width of the kink. Similarly, the transition

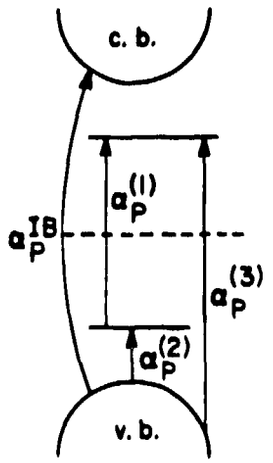

FIGURE 1
The optical transitions allowed to a single polaron. For a charged bipolaron, only $\alpha^{(2)}$ and $\alpha^{(3)}$ are allowed.

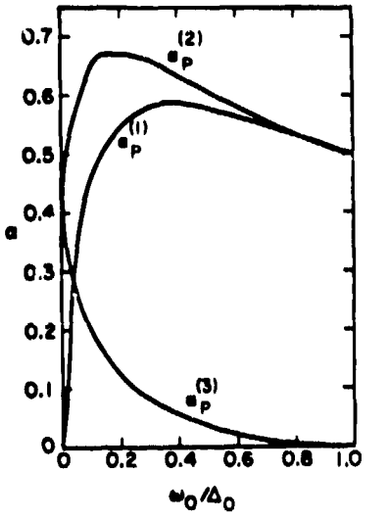

FIGURE 2
The relative integrated intensities for the transitions involving localised levels of polarons/bipolarons plotted as functions of the locations of these levels in the gap.

energy for the charged solitons, $(TE)^{\pm}$, shifts down to $(TE)^{\pm} = \Delta_0 - U/3t_K$. Thus the difference, $(TE)^0 - (TE)^{\pm} = 2U/3t_K$. Importantly, recent optical modulation data on *trans* – $(CH)_x$ [23] reveal a (negative) change in absorption at 1.40 eV associated with (the bleaching of) the K^0 transition (from neutral kinks in the pristine material) and a (positive) change in absorption at 0.45 eV associated with the (appearance of the) $K^{\pm}$ transition. Taking $t_K \simeq 7$, the difference of 0.95 eV implies $U \simeq 10eV (\simeq 4t_0)$. This is well into the intermediate coupling range, where perturbation theory should in fact break down. Indeed, for U of this size the single particle picture itself breaks down, and there is no longer any a priori relation between, for example, the optically excited state of a charged kink ($(K^+)^*$) and the state involving a neutral kink (K^0) plus a hole (-e). One must calculate total energies of both ground and excited N electron states. Nonetheless, as indicated in Section III above, correlated states associated with solitons do exist even for large U, and one can define (and measure) the associated optical transition energies. At present, in the difficult intermediate coupling regime ($U \simeq 4t_0$), there are no definitive theoretical results on optical absorption. For strong coupling, however, one can show that (with U only) $(TE)^0 - (TE)^{\pm} \simeq U$. Thus as the strength of the electron-electron interaction parameter U of Eq. (1) increases, this difference in transition energies crosses over from a (U/t_4) to a U behavior; to understand the detailed nature of this crossover requires accurate many-body calculations for intermediate coupling.

For bipolarons, the corresponding calculations [24] yield, in first order weak e-e coupling (U only), $(TE)^{a_1} \simeq \Delta_0 - \omega_0 - U/3t_{BP}$ and $(TE)^{a_1} \simeq \Delta_0 + \omega_0 - U/3t_{BP}$, so that both absorptions are shifted down. The first non-vanishing changes in intensities are currently being investigated [24], but the essential feature that $I^{a_1} \gg I^{a_1}$ is not expected to change dramatically. This is important, particularly for comparisons to the recent experimental data on (presumed) bipolaron absorption in polythiophene, taken using both doped samples [25] and photoinduced techniques [26]. Both sets of experiments show two peaks [25], occurring at $(TE)^{a_1} \simeq 0.42eV$ and $(TE)^{a_1} \simeq 1.60eV$ in the doped samples [25] and at $(TE)^{a_1} \simeq 0.45eV$ and $(TE)^{a_1} \simeq 1.25eV$ in the photoinduced data [26]. Since the band edge is agreed to be in the range 2.2-2.4 eV, both the existence of two intra-gap absorptions and the fact that the sum of the transitions energies is less than the gap are in agreement with the theoretical expectations for weak e-e interactions. Unfortunately, the experimental integrated intensities of the two absorptions are nearly equal, so that our theoretical expectation fails in an important way. If one ignores this and nonetheless fits the data to the perturbative formulae, one again finds that, due to the $1/t_{BP}$ factors, the value of U lies in the intermediate coupling range. Interestingly, for strong coupling, with both U and V present, the correlated state corresponding to the bipolaron is also expected to have two intra-gap absorptions [24], with $(TE)^{a_1} = V$ and $(TE)^{a_1} = U - 2V$; recall that in this limit the band edge is determined by the e-e interactions and is at $U - V$. Note again the crossover from a U/t_{BP} to a U behavior. Preliminary lowest order estimates [24] suggest roughly equal intensity for the two transitions, with the lower transition expected to be slightly stronger. In view of the uncertainties, it seems premature to attempt a detailed, quantitative interpretation of the experiments, and it is clear that crucial theoretical issues – for instance, the sensitivity of the weak-coupling intensity ratio to effects beyond the scope of the simple 1-d Hamiltonian, and (again) calculations for intermediate coupling – remain open.

5. SUMMARY AND CONCLUSIONS

In the past few years, the role of "correlation effects" in quasi-one-dimensional conductors has gradually come into clearer focus. On the basis of both experimental results and theoretical expectations, it is apparent that these effects can cause important new qualitative and quantitative differences from the single particle picture but that they do not destroy the interesting and important nonlinear excitations predicted by the $H_{e-e} = 0$ models. While theorists debate how best to deal with the (difficult but apparently relevant) intermediate coupling regime, one area of clear

experimental opportunity remains optical absorption. By focusing on coordinated photoinduced/doped sample photoabsorption experiments, time resolved in the sub-picosecond range and on well-characterized, highly oriented samples (so that polarized excitation/probe techniques can be used), the experimentalists can provide perhaps the best insight yet into the excitation structure of quasi-one-dimensional conductors.

REFERENCES

1 C. Fincher et al., Phys. Rev. Lett. 48, 100 (1982); C. S. Yannoni and T. C. Clarke, Phys. Rev. Lett. 51, 1191 (1983).

2 B. S. Hudson, B. Kohler, and K. Schulten, in Excited States, edited by E. C. Lim (Academic, New York, 1982).

3 H. Thomann et al. Phys. Rev. Lett. 50, 533 (1983).

4 S. Kuroda and H. Shirakawa, Solid State Commun. 43, 591 (1982) and these proceedings.

5 B. R. Weinberger, et al. Phys. Rev. Lett. 53, 86 (1984).

6 W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979) and Phys. Rev. B22, 2099 (1980).

7 S. Mazumdar and D. K. Campbell, Phys. Rev. Lett. 55, 2067 (1985); Syn. Metals 13, 163 (1986); and Phys. Rev. B, to appear.

8 N. Nagaosa, Solid State Commun. 57, 179 (1986), and these proceedings.

9 W. P. Su and J. R. Schrieffer, Phys. Rev. Lett. 46, 738 (1981).

10 A continuum version of the model with $t_1 \neq 0$ was first written down by S. A. Brazovskii and N. N. Kirova, JETP Lett. 33, 4 (1981); see also I. V. Krive and S. Roshavskii, JETP Lett. 31, 610 (1981).

11 W. P. Su and J. R. Schrieffer, Proc. Nat. Acad. Sci. 77, 5526 (Physics) (1980).

12 D. K. Campbell and A. R. Bishop, Nuc. Phys. B200, 297 (1982) and p. 195-208 in Nonlinear Problems: Present and Future, A. R. Bishop et al. editors (North Holland, Mathematics Studies vol. 61, 1981).

13 J. L. Bredas, R. R. Chance, and R. Silbey, Mol. Cryst. Liq. Cryst. 77, 319 (1981).

14 D. K. Campbell, T. DeGrand, and S. Mazumdar, Phys. Rev. Lett. 52, 1717 (1984); Mol. Cryst. Liq. Cryst. 118, 41 (1985); J. Stat. Physics, 43, 803 (1986); Phys. Rev. B, to appear.

15 K. R. Subbaswamy and M. Grabowski, Phys. Rev. B24 2168 (1981).

16 J. E. Hirsch, Phys. Rev. Lett. 51, 296 (1983); J. Hirsch and M. Grabowski, Phys. Rev. Lett. 52, 1713 (1984).

17 S Mazumdar and S. N. Dixit, Phys. Rev. Lett. 51, 292 (1983); Phys. Rev. B26, 1824 (1984).

18 Z. G. Soos and S. Ramasesha, Phys. Rev. Lett. 51, 2374 (1983); Phys. Rev. B29, 5410 (1984).

19 E. J. Mele and G. W. Hayden, Proceedings of the ICSM'86, to be published (Springer, 1986).

20 S. Kivelson, T.-K. Lee, Y. R. Lin-Liu, I. Peschel, and Lu Yu, Phys. Rev. B25, 4173 (1982).

21 K. Fesser, A. R. Bishop, and D. K. Campbell, Phys. Rev. B27, 4804 (1983).

22 D. Baeriswyl, D. K. Campbell, and S. Mazumdar, Phys. Rev. Lett. 56, 1509 (1986).

23 Z. Vardeny and J. Tauc, Phys. Rev. Lett. 54, 1844 (1985).

24 D. Baeriswyl, D. K. Campbell, and S. Mazumdar, Phys. Rev. B, to be published.

25 W. Harbeke et al., Solid State Commun. 55, 419 (1985). These authors also observe, at low doping levels, a peak possibly associated with the $2\omega_0$ polaron absorption (called α_1 in the text).

26 Z. Vardeny et al., Phys. Rev. Lett. 55, 671 (1986).